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# POLY(NiPAAm-co-IA) HYDROGELS SYNTHESIZED BY γ-IRRADIATION: SWELLING BEHAVIOR IN WATER

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**Abstract**

In this study, N-isopropylacrylamide/itaconic acid copolymeric (poly(NiPAAm-co-IA)) hydrogels were synthesized by γ-irradiation induced simultaneous polymerization and crosslinking of monomers. The influence of comonomer concentration (IA) on the swelling behavior in water was investigated. The results showed that values of network parameters increase with an increase of IA, and that the swelling transport mechanism is a non-Fickian transport.

**Introduction**

Hydrogels are a class of polymeric materials which have been utilized in a wide range of application due to easily adjustable properties. Stimuli-sensitive, also called intelligent polymers, change their structure and physico-chemical properties in response to physical or chemical stimuli. These smart polymers have a vast potential for applications in pharmaceutical technology, biotechnology industry, and in solving environmental problems. Among them, temperature- and pH-sensitive polymers are the most frequently studied [1].

PolyNiPAAm is the best-known temperature-sensitive polymer that attracts huge interest in biomedical applications due to well-defined lower critical solution temperature (LCST) in water around 32 $^{o}$C, which is close to the body temperature. The temperature-sensitive networks containing ionizable functional groups exhibit pH-sensitivity. With the increase of ionizable groups, the volume change at the transition increases because of increasing electrostatic interaction between the same charged groups and the transition temperature rises. In recent years, a series of papers has been published about hydrogels from the copolymers of acrylamide and diprotic itaconic acid (IA) and maleic acid (MA), and showed that the use of even very small quantities of diprotic acid proved to impart remarkable properties to the hydrogels of starting monomers and/or homopolymers [2].

γ-irradiation induced synthesis has been recognized as highly suitable tool for crosslinking of polymeric hydrogels. This method is relatively simple and do not require addition of any extra materials such as initiator and/or crosslinker. Moreover, the degree of crosslinking, which strongly determines the extent of swelling in hydrogels, can be controlled easily by varying the irradiation dose. Therefore, γ-irradiation is found to be very useful in preparing hydrogels for medical applications, where even a small contamination is undesirable [1-3].

The aim of this work was to synthesized polyNiPAAm and poly(NiPAAm-co-IA) hydrogels by γ-irradiation induced simultaneous polymerization and crosslinking, and to investigate the influence of IA concentration on network parameters and swelling behavior in water, as well as to determine diffusion properties of hydrogels.

## Experimental

The NiPAAm monomer was used as a base monomer in the synthesis of hydrogels, while the IA was used as comonomer. Solution of NiPAAm (10 wt.%) was prepared in distilled water. Different amounts of IA were added to 5 ml of NiPAAm solution in order to obtain NiPAAm/IA mass ratios 100/0, 98.5/1.5, 97/3 and 95.5/4.5. Monomer solutions were bubbled with argon for 20 min, to remove oxygen, and exposed to γ-irradiation ($^{60}$Co source) up to absorbed dose of 50 kGy, at a dose rate of 0.6 kGy/h. The obtained hydrogels were immersed in an excess of deionized water, which is changed every day during one week, to remove uncrosslinked polymer and/or residual monomers, and dried at room temperature. Dynamic swelling measurement was performed in deionized water at 25 ± 1 $^{o}$C, using dry gels (xerogels). The swelling process was monitored gravimetrically.

## Results and Discussion

When a xerogel is brought into contact with a solution, the solution diffuses into the network and volume phase transition occurs, resulting in the expansion of the hydrogel. Diffusion involves the migration of fluid into pre-existing or dynamically formed spaces between the hydrogel chains. The capacity of swelling is one of the most important parameters for evaluation the properties of hydrogels. As can be seen from Table 1, the characteristic parameters obtained from swelling measurement in water of an ionic hydrogel strongly depend on the concentration of ionizable groups in network. The results showed that the equilibrium swelling degree ($SD_{eq}$) of poly(NiPAAm-co-IA) hydrogels increase as the comonomer concentration increases because of increasing the electrostatic interactions of the neighboring carboxylate groups in IA in the hydrogels [4]. Moreover, the values of network parameters, average molar mass between the network crosslinks ($M_c$) and distance between the macromolecular chains ie. pore size ($\xi$), also increase with increasing amount of IA, whereas the xerogel densities decrease.

**Table 1**. Characteristic parameters obtained from swelling measurement in water at 25 $^{o}$C. (S0) - (S3) are symbols of the synthesized hydrogels.

| *poly (NiPAAm/IA)* | $SD_{eq}$ | $M_c$ *(g/mol)* | $\xi$ *(nm)* | $\rho_{xg}$ *(g/cm$^3$)* | *k (1/min)* | *n* | $D\times10^5$ *(cm$^2$/min)* |
|---|---|---|---|---|---|---|---|
| 100/0 (S0) | 9.2 | 627 | 3.7 | 0.91 | 0.024 | 0.52 | 0.23 |
| 98.5/1.5 (S1) | 29.1 | 2905 | 10.9 | 0.80 | 0.014 | 0.64 | 1.14 |
| 97/3 (S2) | 37.1 | 4041 | 13.8 | 0.79 | 0.013 | 0.65 | 1.21 |
| 95.5/4.5 (S3) | 52.6 | 7034 | 20.4 | 0.78 | 0.012 | 0.66 | 1.28 |

To obtain a more quantitative understanding of the nature of the sorption kinetic in poly(NiPAAm-co-IA) hydrogels, the initial swelling data were fitted to

equation $M_t/M_{eq} = k\ t^n$, were $M_t$ is the amount of absorbed water in time $t$, $M_{eq}$ is the maximum absorbed amount, $k$ is a constant incorporating characteristics of macromolecular network system and the penetrant, $n$ is the diffusion exponent, which is indicative of the transport mechanism. This equation is valid for initial stage of swelling ie. for the first 60 % of the normalized solvent uptake. The characteristic constants $n$ and $k$ were calculated from the slope and intercept, respectively, of the linear parts of logarithmic form of kinetic equation of swelling. The obtained results are presented in Table 1, and indicated that hydrogel systems show non-Fickian or anomalous diffusion ($0.5 < n < 1$) when the rates of diffusion and polymer chain relaxation are comparable [5].

The study of diffusion phenomena of water in hydrogels is important because that clarifies the polymers behavior. For hydrogel characterization, the diffusion coefficients ($D$) can be calculated by using the equation $D^n = (k/4)\ (\pi/r^2)$, were $r$ is the radius of gel disc. The $D$ values are also presented in Table 1. The diffusion coefficients increase with an increase in IA content in the hydrogels. This is due to the hydrophilicity for these copolymeric hydrogels in the order of (S0) < (S1) < (S2) < (S3), and the more hydrophilic groups in the gel, the easier the diffusion for water molecules [1,2].

**Conclusion**

The poly(NiPAAm-co-IA) hydrogels were successfully synthesized by γ-irradiation. The equilibrium swelling degree ($SD_{eq}$) of copolymeric hydrogels increase with an increase of IA content, due to incorporation of more specific acid groups into the network and consequent higher swelling capacity of gels. The network parameters $M_c$ and $\xi$ also increase with increasing amount of IA, whereas the xerogel densities decrease. In the diffusion transport mechanism study, the results indicate that the swelling transport mechanism is a non-Fickian transport. The diffusion coefficients ($D$) of poly(NiPAAm-co-IA) hydrogels increase with an increase of IA content, so the water molecule easily infiltrates into hydrogels for gels containing higher IA content.

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